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Supporting Information

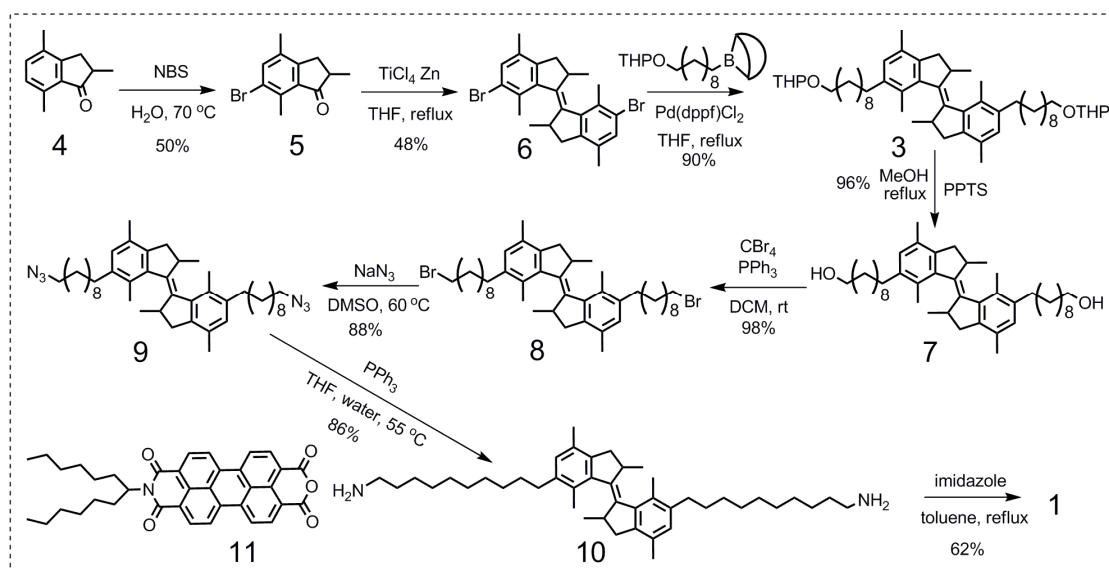
Photoswitchable Intramolecular H-stacking of Perylenebisimide

Jiaobing Wang, Artem Kulago, Wesley R. Browne* and Ben L. Feringa*

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Synthesis



5. To a solution of compound **4**¹ (700 mg, 4.0 mmol) in 40 mL acetonitrile was added aqueous H₂SO₄ (15%, 30 mL) at room temperature followed by NBS (750 mg, 4.16 mmol). The solution was stirred at 70 °C for 14h. After cooling to room temperature, the mixture was poured into 200 mL water and extracted with dichloromethane (DCM, 2 × 100 mL). The combined organic phase was dried and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using pentane/DCM (3/1) as the eluant affording 510 mg (50%) of **5** as a yellow solid. mp: 78.1-78.8 °C. ¹H NMR (CDCl₃): δ = 7.54 (s, 1H), 3.18 (dd, *J* = 17.2, 7.6 Hz, 1H), 2.67 (m, 4H), 2.48 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.28 (s, 3H), 1.30 (d, *J* = 7.6 Hz, 3H). ¹³C NMR (CDCl₃): 210.2, 152.6, 138.1, 138.0, 136.0, 135.0, 134.5, 125.2, 42.5, 33.0, 17.4, 16.7. HRMS: *m/z* calcd for C₁₂H₁₄BrO [M+H]⁺: 253.0233; found: 253.0216.

trans-6.² To a suspension of zinc powder (2.0 g, 31.3 mmol) in 60 mL dry THF was added 1.63 mL TiCl₄ at 0 °C. The mixture was heated at reflux under N₂ for 2h. After cooling down to room temperature, compound **5** (2.0 g, 8.0 mmol) was added. The mixture was again heated at reflux under N₂ for 12h. After cooling to room temperature, the mixture was directly charged onto a silica gel column using DCM as eluant to remove the metal salts. The product was further purified by chromatography on silica gel using pentane/DCM (3/1) as eluant. The product was recrystallized from methanol/ dichloromethane, yielding **trans-6** as a white solid. mp: 184.1-185.6 °C. ¹H NMR (CDCl₃): δ = 7.28 (s, 2H), 2.84 (m, 2H), 2.59 (dd, *J* = 14.7, 5.4 Hz, 2H), 2.47 (s, 6H), 2.24 (d, *J* = 14.7 Hz, 2H), 2.18 (s, 6H), 1.11 (d, *J* = 6.0 Hz, 6H). ¹³C NMR (CDCl₃): 142.8, 142.4, 141.8, 133.7, 131.8, 131.0, 123.8, 42.3, 39.0, 23.2, 19.0, 18.1. HRMS: *m/z* calcd for C₂₄H₂₆Br₂ [M-e]⁺: 474.0381; found: 474.0357.

7. PPTS (100 mg, 0.4 mmol) and **3** (100 mg, 0.126 mmol) were dissolved in 15 mL MeOH. The mixture was heated at 75 °C in a sealed flask under N₂ for 2h. Then the mixture was cooled down and the solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography using pentane/ethyl acetate (100/50) as the eluant affording 76 mg (96%) of **7** as a colorless oil. ¹H NMR (CD₂Cl₂): δ = 6.86 (s, 2H), 3.64 (t, *J* = 5.6 Hz, 4H), 2.90-2.78 (m, 2H), 2.73-2.53 (m, 6H), 2.38 (s, 6H), 2.24-2.14 (m, 8H), 1.73-1.26 (m, *J* = 3, 2H), 1.10 (d, *J* = 5.6 Hz, 6H). ¹³C NMR (CD₂Cl₂): δ 141.90, 139.9, 139.6, 131.2, 129.3, 128.8, 63.0, 42.5, 38.9, 33.6, 33.1, 31.0, 30.1, 29.8, 26.0, 19.0, 18.1. HRMS: *m/z* calcd for C₄₄H₆₇O₂ [M-H]⁻: 627.5136; found: 627.4759.

8. Triphenylphosphine (192 mg, 0.73 mmol) and CBr₄ (121 mg, 0.36 mmol) were added to a solution of **7** (70 mg, 0.11 mmol) in 10 mL dry DCM. The mixture was stirred at room temperature for 20 min. Then the solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography using pentane/DCM (3/1) as the eluant affording 82 mg (98%) of **8** as a colorless oil. ¹H NMR (CD₂Cl₂): δ = 6.87 (s, 2H), 3.45 (t, *J* = 5.6 Hz, 4H), 2.86-2.78 (m, 2H), 2.70-2.55 (m, 6H), 2.39 (s, 6H), 2.21 (d, *J* = 14.4 Hz, 2H), 2.18 (s, 6H), 1.94-1.82 (m, 4H), 1.70-1.25 (m, 28H), 1.07 (d, *J* = 5.6 Hz, 6H). ¹³C NMR (CDCl₃) δ 143.8, 143.7, 141.8, 141.5, 133.0, 131.3, 130.7, 44.4, 40.9, 36.4, 35.5, 35.0, 33.2, 33.0, 32.0, 31.7, 31.6, 31.0, 30.3, 21.0, 20.1. HRMS: *m/z* calcd for C₄₄H₆₇Br₂ [M+H]⁺: 755.3593; found: 755.3595.

9. NaN₃ (200 mg, 3.07 mmol) was added to a solution of **8** (50 mg, 0.066 mmol) in 15 mL DMSO. The mixture was stirred at 60 °C under N₂ for 15 h. After cooling to room temperature, the mixture was poured into 100 mL water and extracted with DCM (2 × 50 mL). The combined organic phase was dried and the solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography using pentane/DCM (3/1) as the eluant affording 40 mg (88%) of **9** as a colorless oil. ¹H NMR (CDCl₃): δ = 6.88 (s, 2H), 3.28 (t, *J* = 6.8 Hz, 4H), 2.90-2.81 (m, 2H), 2.73-2.55 (m, 6H), 2.40 (s, 6H), 2.24-2.14 (m, 8H), 1.70-1.25 (m, 32H), 1.10 (d, *J* = 5.6 Hz, 6H). ¹³C NMR (CDCl₃) δ 142.0, 141.9, 139.9, 139.8, 131.1, 129.5, 128.8, 51.7, 42.5, 39.1, 33.7, 31.0, 30.2, 30.0, 29.8, 29.4, 29.1, 27.0, 19.3, 18.5. HRMS: *m/z* calcd for C₄₄H₆₇N₂ [M-N₄+H]⁺: 623.5308; found: 623.5295.

10. Triphosphine (460 mg, 1.75 mmol) was added to a solution of **9** (300 mg, 0.44 mmol) in 50 mL dry THF. The mixture was stirred at room temperature for 3h. Then 3 mL water was added and the mixture was stirred at 55 °C under N₂ for 15 h. After cooling to room temperature, the solvent was evaporated under vacuum. The residue was dissolved in 100 mL DCM. After the addition of 2% aqueous hydrochloric acid (100 mL), a white precipitate (hydrochloric salt of **10**, used in the next reaction, 264 mg, 86%) was obtained. The product was neutralized with saturated K₂CO_{3(aq)} and extracted with DCM followed by solvent evaporation, affording **10** as a colorless oil. ¹H NMR (CDCl₃): δ = 6.86 (s, 2H), 2.91-2.82 (m, 2H), 2.77-2.54 (m, 10H), 2.37 (s, 6H), 2.23-2.10 (m, 8H), 1.70-1.25 (m, 32H), 1.10 (d, *J* = 5.6 Hz, 6H). ¹³C NMR (CDCl₃) δ 142.0, 141.9, 139.9, 139.8, 131.1, 129.4, 128.7, 42.5, 39.1, 33.7, 31.0, 30.2, 29.9, 29.85, 29.8, 29.8, 27.2, 19.3, 19.2, 18.5. HRMS: *m/z* calcd for C₄₄H₇₁N₂ [M+H]⁺: 627.5612; found: 627.5622.

1. Hydrochloric salt of **10** (30 mg, 0.043 mmol), imidazole (200 mg, 2.94 mmol), and **11** (70.0 mg, 0.122 mmol) were added to 10 mL dry toluene. The mixture was heated at 120 °C under N₂ in a sealed flask for 4h. After cooling to room temperature, the mixture was directly purified by silica gel chromatography using CHCl₃ as eluant, yielding **1** as a red solid (62%, 46 mg, 0.026 mmol). mp 163.1-164.2 °C. ¹H NMR (CDCl₃): δ = 8.62-8.38 (m, 16H), 6.84 (s, 2H), 5.24-5.10 (m, 2H), 4.14 (t, *J* = 7.2 Hz, 4H), 2.86-2.73 (m, 2H), 2.70-2.51 (m, 6H), 2.37 (s, 6H), 2.33-2.12 (m, 12H), 1.96-1.82 (m, 4H), 1.80-1.68 (m, 4H), 1.66-1.20 (m, 60H), 1.07 (d, *J* = 6.3 Hz, 6H), 0.83 (t, *J* = 6.3 Hz, 12H). ¹³C NMR (CDCl₃): 163.3, 141.8, 141.7, 139.9, 139.5, 134.6, 134.3, 131.1, 129.3, 128.8, 126.4, 126.3, 123.3, 123.1, 40.7, 38.9, 33.5, 32.5, 32.0, 31.0, 29.9, 29.7, 29.5, 29.4, 28.2, 27.3, 27.1, 22.8, 19.0, 18.1, 14.0. HRMS: *m/z* calcd for C₁₁₈H₁₃₇N₄O₈ [M+H]⁺: 1739.0465; found: 1739.0471.

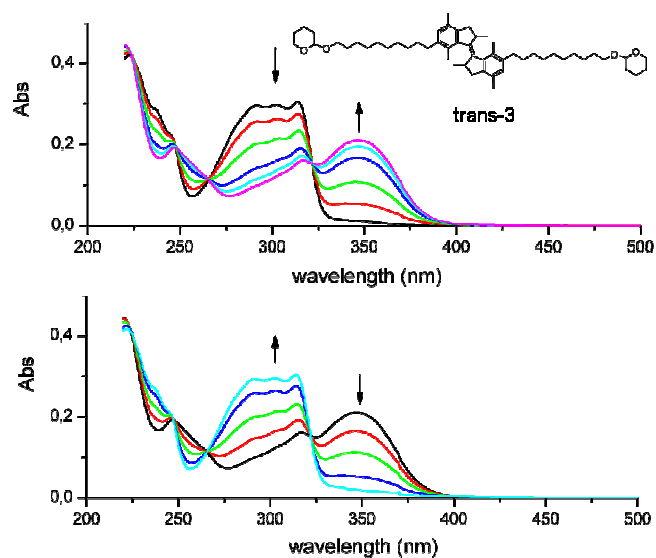


Figure S1. Changes to the UV-vis absorption spectrum of *trans*-**3** upon irradiation at 312 nm (top), 50 s, $\Phi_{iso} = 0.159$, in THF at 20 °C and the reversal of the spectral changes (bottom) upon irradiation at 365 nm, 70 s, $\Phi_{iso} = 0.078$.

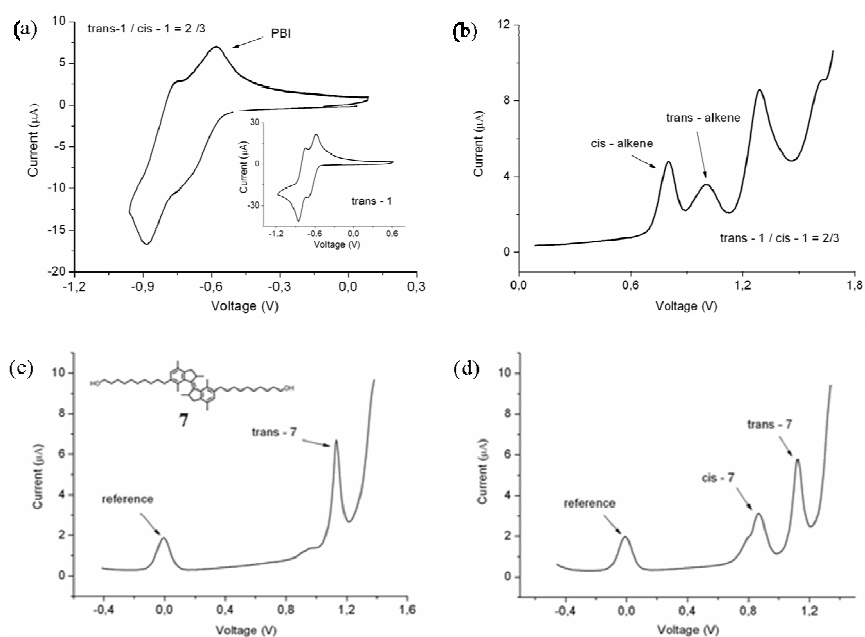


Figure S2: Cyclic (a) and differential pulse (b) voltammetry of compound **1** (trans-1/cis-1 = 2/3) in $\text{CH}_2\text{Cl}_2/0.1 \text{ M TBAPF}_6$ at 20 °C. Differential pulse voltammetry of the reference compound **7** (c, trans-**7**, d, trans-**7**/cis-**7** = 1/1) was measured to assign the oxidation processes due to the overcrowded alkene.

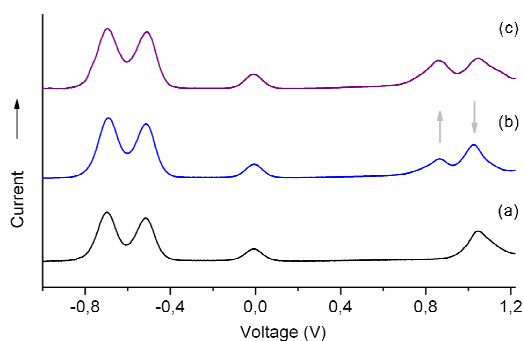


Figure S3. Differential pulse voltammetry of trans-2 (1 mM) before (a) and after (b, c) UV irradiation at 312 nm in CH₂Cl₂/0.1 M TBAPF₆ at 20 °C. The oxidation potential of the overcrowded alkene decreases upon trans→cis isomerization.

Gibbs energy (ΔG_{ET}) of photo-induced electron transfer (PET) is calculated using the Rehm Weller Equation

$$\Delta G_{ET} = e[E_{ox}(OA) - E_{red}(PBI)] - E_{00} - \frac{e^2}{4\pi\epsilon_0\epsilon_s R_{CC}} - \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{r^+} + \frac{1}{r^-} \right) \left(\frac{1}{\epsilon_{ref}} - \frac{1}{\epsilon_s} \right)$$

$$\frac{e^2}{4\pi\epsilon_0} = 2.307 \times 10^{-28} \text{ J m}$$

where $E_{ox}(OA)$ is the oxidation potential of the overcrowded alkene (OA) $E_{red}(PBI)$: the first reduction potential of the PBI unit (-0.58 V), $E_{ox}(trans-OA) = +1.01$ V, $E_{ox}(cis-OA) = +0.80$ V, (Figure S2b). E_{00} : the energy of the S1→Sn excited state (2.34 eV). R_{CC} : the distance (19.7 Å) between the centers of the electron donor (OA) and acceptor (PBI), r^+ and r^- : the effective ionic radii of the donor and acceptor radical cation and anion, respectively and ϵ_{ref} and ϵ_s : the dielectric constant of the solvent used to determine redox potentials and the solvent used for spectroscopic measurements respectively (8.93 for CH₂Cl₂). All electrochemical data was obtained in the same solvent/electrolyte and hence the last term reduces to zero.

The quantum yield of trans-1 is lower, 30%, than that of trans-2. This might be ascribed to interaction with the PBI in the trans-state, resulting from the back-folding of the flexible C-10 alkyl chains. This is indicated by the higher A^{0-1}/A^{0-0} ratio of trans-1 (0.71) than that of trans-2 (0.63, a value typical for non-aggregated PBI), see Figure 2a, c. But this interaction is very much less than that of H-stack in the PSS cis-state ($A^{0-1}/A^{0-0} = 1.18$), where it is the dominant state.

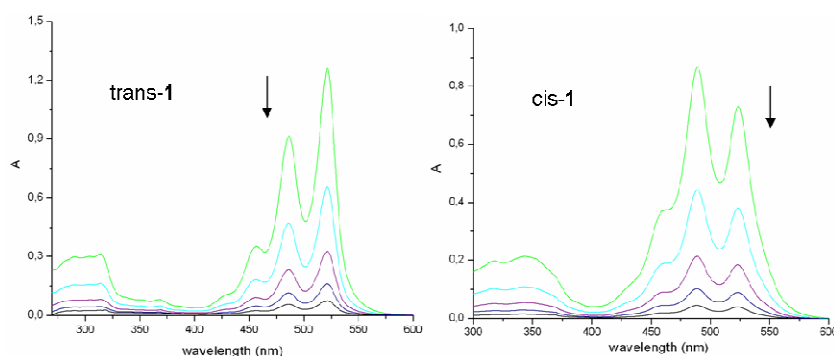


Figure S4: Absorption spectra of compound 1 at several concentrations. No change on the spectral shape is observed during dilution from 1.0×10^{-4} to 6.3×10^{-6} M, indicating the absence of intermolecular interactions.

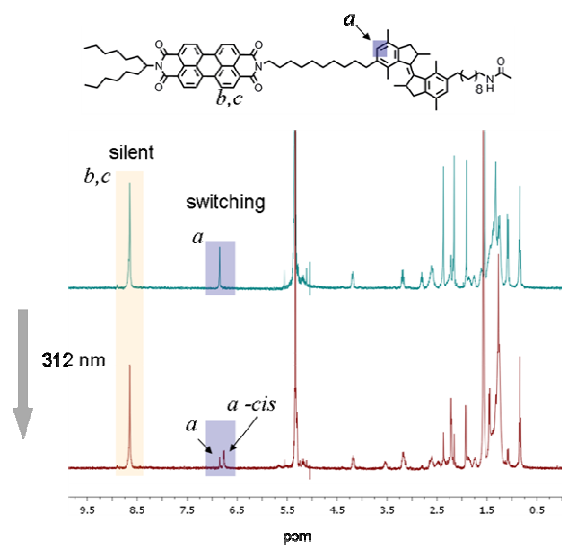


Figure S5. ^1H NMR spectroscopy of *trans*-**2** (Fig. a) before (top) and after (bottom) irradiation at 312 nm in CH_2Cl_2 at 20 °C.

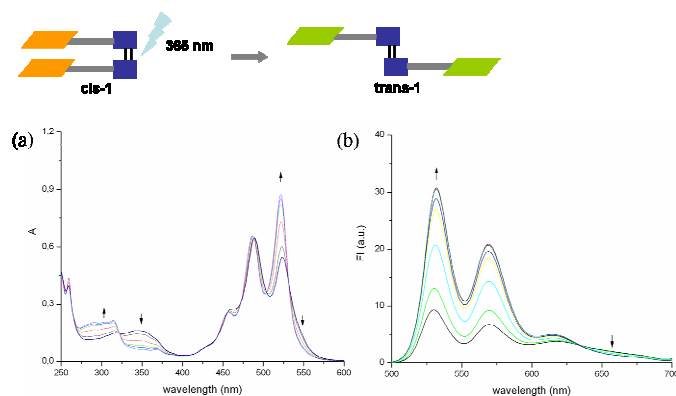


Figure S6: Reversal absorption (a) and fluorescence (b, $\lambda_{\text{ex}} = 455$ nm) spectral changes of compound **1** upon irradiation at 365 nm in THF at 20 °C, and a schematic presentation of the *cis*→*trans* switching process.

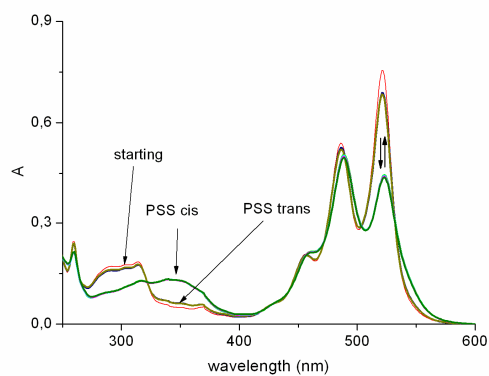


Figure S7. Absorption spectral changes of compound **1** upon alternate irradiation at 312 and 365 nm in THF.

At the photo stationary state, based on Figure S7, mole ratio (α_1 , α_2) of the isomer was calculated using the following two equations:

$$1) A^{\text{cis}} \times \alpha_1 + A^{\text{trans}} \times (1 - \alpha_1) = {}^{\text{pss}}A^{\text{trans} \rightarrow \text{cis}}$$

$$2) A^{\text{trans}} \times \alpha_2 + A^{\text{cis}} \times (1 - \alpha_2) = {}^{\text{pss}}A^{\text{cis} \rightarrow \text{trans}}$$

A^{cis} : absorbance of the cis isomer, which can be calculated using equation 1; α_1 : mole ratio of the cis isomer, 81%, determined from the $^1\text{H-NMR}$ spectroscopy; A^{trans} : absorbance of the trans isomer (starting line, Figure S7); ${}^{\text{pss}}A^{\text{trans} \rightarrow \text{cis}}$: absorbance of the photo stationary state (trans \rightarrow cis). ${}^{\text{pss}}A^{\text{cis} \rightarrow \text{trans}}$: absorbance of the photo stationary state (cis \rightarrow trans); α_2 : mole ratio of the trans isomer.

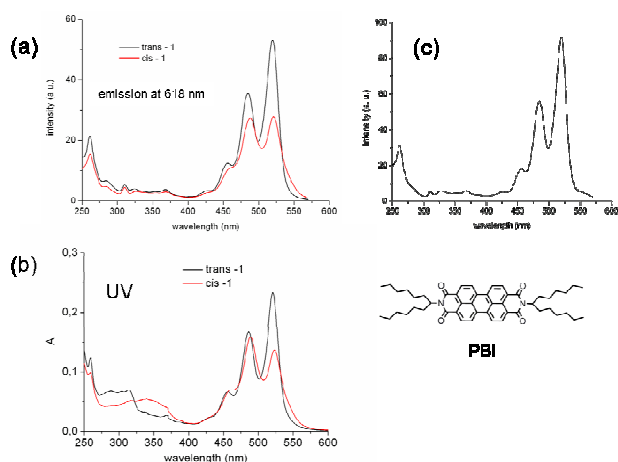


Figure S8: Excitation (a, $\lambda_{\text{em}} = 618 \text{ nm}$) and absorption (b) spectra of compound **1**. For comparison, the excitation spectrum of a control compound PBI (c) is also presented.

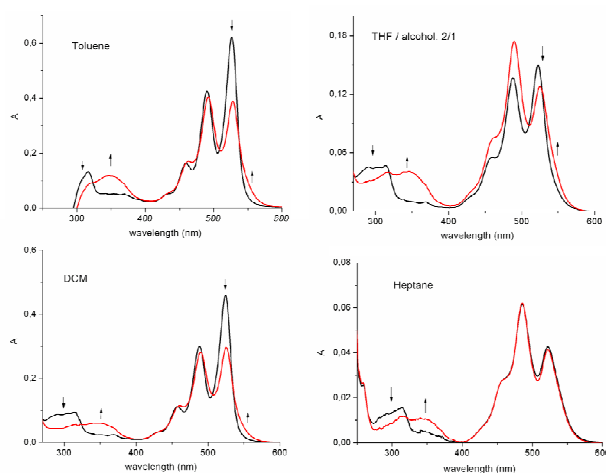


Figure S9. Absorption spectral changes of compound **1** upon alternate irradiation at 312 nm in different solvents.

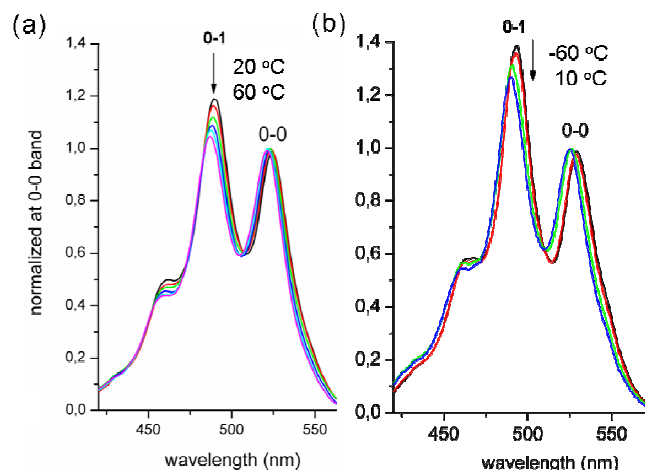


Figure S10. Absorption spectra of compound **1** at different temperatures. In the trans-state (a), the 0-1 band is lower than 0-0 band at different temperatures, indicating a monomer-type PBI chromophore. In the cis-state (b, c), the 0-1 band is higher than 0-0 band at different temperatures indicating a H-type PBI stacking.

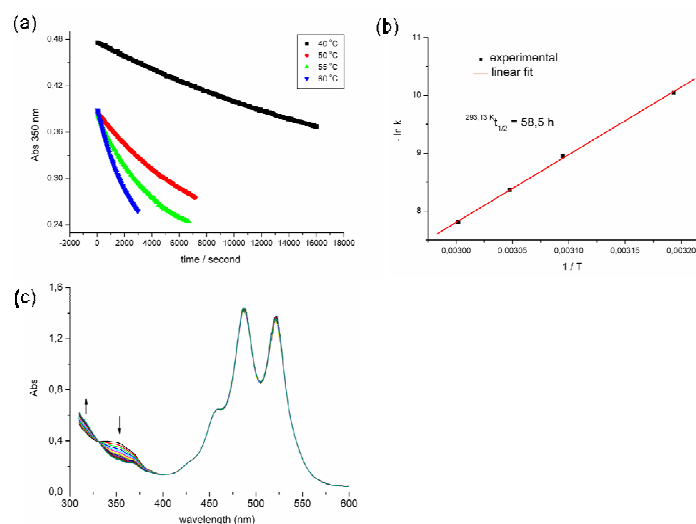
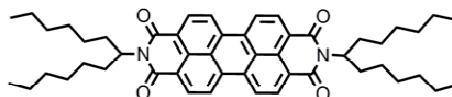


Figure S11. Thermal isomerization of the overcrowded alkene from unstable cis- to stable cis-state followed by absorption changes at 350 nm at four different temperatures (40, 50, 55 and 60 °C, Fig. 11a). A half life of 58.5 h at 20 °C was determined (Fig 11b, $E_a = 97.3$ kJ/mol). UV-vis spectral changes of cis-**1** at 60 °C for 20 min. (Fig 11c). Decreasing of the absorption at 350 nm indicates the isomerization the overcrowded alkene from unstable cis- to stable cis-state, see ref. 2. Thermal isomerization of the overcrowded alkene does not have noticeable effect on the PBI interactions.

Determination of Quantum yield of fluorescence:

The fluorescence quantum yield was determined by comparison of the integrated area (480 nm-720 nm) of the emission ($\lambda_{ex} = 455$ nm) spectrum of the sample with that of the

reference PBI compound (in toluene, $^{PBI}\Phi_f = 1$, Würthner, F. *Chem. Commun.* **2004**, 1564-1579).



PBI

Determination of Quantum yield of photoisomerization:

3 mL of aqueous ferrioxalate (0.006 M) solution (0.05 M H₂SO₄) was transferred to a cuvette and irradiated with the monochromated (5 nm bandwidth) output of the Xe lamp of the JASCO FP-6200 spectrophotometer. The concentration was such that the absorbance at the excitation wavelength was above 3. 2 mL of the irradiated solution were mixed with 2 mL of aqueous phenanthroline solution (5 mM) and 1 mL of CH₃COONa/H₂SO₄ buffer (pH = 3.5, 0.6 M) in a 20 mL graduated flask and diluted to 20 mL with water. The solution was kept in the dark for 1 h, and the absorption spectrum was measured. The absorbance at 510 nm (absorption of the Fe²⁺-phenanthroline complex, $\epsilon_{510\text{ nm}} (1.11 \times 10^4 \text{ l/mol}\cdot\text{cm})$) was recorded. As a control, 2 mL of the non-irradiated ferrioxalate (0.006 M) solution was treated in exactly the same way. The spectrum was used for baseline correction. The procedure was repeated using several irradiation times (10-60 min) and a plot of the absorbance at 510 nm as a function of time was used to determine the photon flux together with the reported quantum yields ($^{312\text{nm}}\Phi_{\text{pr}} = 1.24$, $^{365\text{nm}}\Phi_{\text{pr}} = 1.21$).

For compounds **1-3**, quantum yields were measured in THF (at 0.2 mM, the monochromated light was totally absorbed). 2.2 mL of solution was subjected to irradiation for different times (10-60 min). The irradiated samples were diluted and the UV-vis absorption spectra recorded. Plotting the absorbance at 350 nm (absorption of the overcrowded alkene in the cis-state) as a function of time provided the change in absorbance ΔA_{350} at 350 nm at irradiation time t_2 . Non-irradiated samples were used for baseline correction.

References

- (1) Kaminsky, W.; Rabe, O.; Schauwienold, A.-M.; Schupfner, G. U.; Hanss, J.; Kopf, J. *J. Organomet. Chem.* **1995**, 497, 181.
- (2) Pollard, M. M.; Meetsma, A.; Feringa, B. L. *Org. Biomol. Chem.* **2008**, 6, 507-512.
- (3) Santangelo, E. M.; Coracini, M.; Witzgall, P.; Correa, A. G.; Unelius, C. R. *J. Nat. Prod.* **2002**, 65, 909-915.

